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Collective molecular rotation in water and other simple liquids

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Abstract

Hyper-Rayleigh light scattering measurements of molecular motion in several liquids find that the orientations of the molecules are correlated over macroscopic distances. Such collective molecular rotation occurs in addition to the usually observed, highly localized, diffusive mode of molecular reorientation. Long range correlation of molecular orientation may have significant unrecognized effects on the structure and properties of liquids. © 2000 Elsevier Science B.V. All rights reserved.

Rotation and vibration of molecules in a liquid are usually viewed as local excitations, as opposed to the delocalized, propagating waves or phonons which characterize atomic motion in pure crystals. According to this view molecules in a liquid reorient by rotational diffusion, and orientational correlations extend only a few molecular diameters [1,2]. However, theory allows both diffusive and propagating hydrodynamic modes [3]. In the case of density fluctuations, thermal diffusion and sound waves result in the well-known Rayleigh and Brillouin peaks in the spectrum of light scattered by a liquid [1–4]. In contrast, molecular polar orientation waves in a liquid were first observed and thoroughly analyzed in recent hyper-Rayleigh scattering (HRS) measurements for acetonitrile [5]. Those measurements find that the HRS spectrum for acetonitrile is dominated by the delocalized mode of molecular reorientation, but do not say whether acetonitrile is exceptional or typical in this regard. Here we report less extensive

HRS measurements for several liquids including water, which test for the presence of delocalized molecular rotation modes. We find that collective reorientation is typical for liquids composed of small dipolar molecules. Our finding suggests that rotational diffusion is not an adequate description of molecular reorientation in most liquids, and that orientational correlation between molecules may extend much farther than previously envisioned.

To investigate molecular reorientation in several representative liquids, we measured the polarization dependence of HRS in the 90° scattering geometry with linearly polarized light [5,6]. The beam from a pulsed Nd:YAG laser operating at $\lambda = 1064$ nm is focused into the filtered liquid sample contained in a fluorimeter cuvette, the light scattered into a 0.2 sr solid angle is collected with a lens, and a 25 cm^{-1} wide spectral band centered at $\lambda = 532$ nm is selected with a grating spectrometer. Only orientational excitations contribute significantly to HRS in this spectral band. The polarization of the incident laser beam is controlled using a prism polarizer and Soleil–Babinet compensator, while the polarization of the collected light is analyzed with a sheet polar-

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izer followed by a polarization scrambler. Light polarized parallel (perpendicular) to the horizontal scattering plane is denoted H (V). The polarization combinations considered are labeled VV, HV, VH, and HH, where the incident polarization is given by the first letter and the scattered polarization detected is given by the second letter.

Fig. 1 shows the scattering process. A pair of incident photons with wavevector k_i are absorbed and a photon with wavevector k_s is emitted. Momentum is conserved by the recoil of the molecules. Since individual molecules respond to the electric field and not the wavevector of the light, the scattered intensity from randomly oriented molecules in an isotropic fluid is the same by symmetry for HV, VH, and HH polarizations (the three mutually perpendicular combinations of incident and scattered fields). The situation is different if molecular orientations are correlated in the form of a propagating wave with wavevector $K = 2k_i - k_s$, extending over distances comparable to or larger than the light wavelength. Scattering from this momentum-conserving collective excitation is greatly enhanced because the light scattered from the molecules in a large volume constructively interferes. The propagating polar modes with wavevector K which can contribute to HRS are two transverse optical (TO) modes and one longitudinal optical (LO) mode [5,7]. Scattering from a collective mode with this particular K breaks the symmetry of the process with respect to the HV, VH, and HH polarizations. Table 1 shows the predicted polarization dependence of HRS for
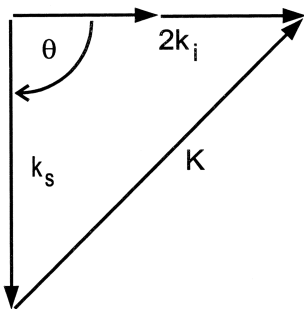
Table 1
HRS polarization dependence for local and nonlocal modes. The numerical values of P^2 and R^2 depend on molecular structure

Polarization	HRS intensity		
	Local	TO	LO
VV	P^2	R^2	0
HV	1	1	0
VH	1	1/2	1/2
HH	1	1/2	1/2

local, TO and LO modes of molecular reorientation [5].

The polarization dependence predicted in Table 1 can be used to detect the presence of non-local contributions to HRS [5,7]. The ratio $I_{HV}/I_{VH} = 1$, 2, or 0 for local, TO, or LO modes, respectively. Significant deviation from $I_{HV}/I_{VH} = 1$ signals the presence of non-local modes. The other polarization ratios alone are not decisive, since $I_{HH}/I_{VH} = 1$ in all cases, while I_{VV}/I_{VH} varies with molecular structure. Table 2 shows the measured HRS polarization ratios for eight liquids, corrected for the effects of the finite collection angle [8]. The corrections are proportional to $(I_{VV}/I_{VH} - 1)$ and are the same for I_{HV}/I_{VH} and I_{HH}/I_{VH}. Therefore, the I_{HH}/I_{VH} measurements given in the third column of Table 2 serve as a check for systematic errors in the I_{HV}/I_{VH} measurements given in the second column. No significant deviations from $I_{HH}/I_{VH} = 1$ are observed. Examining the second column of Table 2, one sees evidence for significant deviations from local mode behavior for all the liquids except CCl_4 and methanol. TO modes contribute for acetonitrile and nitrobenzene, while LO modes contribute for chloroform,

Fig. 1. HRS is the non-linear scattering process where two photons (ω, k_i) are absorbed and one photon $(2\omega - \Omega, k_s)$ is emitted. Energy and momentum in the scattering process is conserved by an excitation of the liquid with frequency Ω and wavevector K. In this experiment the scattering angle $\theta = 90°$.

Table 2
HRS polarization ratios measured for several molecular liquids at 23°C. Error bars are 1 SD

Liquid	I_{HV}/I_{VH}	I_{HH}/I_{VH}	I_{VV}/I_{VH}
CH_3CN	1.24 ± 0.02	0.99 ± 0.02	11.2 ± 0.2
$C_6H_5NO_2$	1.08 ± 0.01	1.00 ± 0.01	7.6 ± 0.2
CCl_4	1.00 ± 0.01	0.99 ± 0.01	1.9 ± 0.1
CH_3OD	0.99 ± 0.02	0.98 ± 0.02	2.2 ± 0.1
$CDCl_3$	0.90 ± 0.02	0.99 ± 0.02	2.1 ± 0.1
D_2O	0.88 ± 0.02	0.97 ± 0.02	6.3 ± 0.2
CD_3NO_2	0.87 ± 0.02	0.98 ± 0.02	3.0 ± 0.1
$(CH_3)_2CO$	0.79 ± 0.02	0.96 ± 0.03	2.2 ± 0.2

water, nitromethane, and acetone. It is possible that both TO and LO modes contribute for CCl_4 and methanol and that $I_{HV}/I_{VH} = 1$ is observed because the two contributions cancel. Although the 10–20% deviations observed for the spectrally averaged polarization ratios are not very dramatic, much larger effects are expected for spectrally resolved measurements. For acetonitrile, the one example where analysis of combined spectral and polarization measurements has been carried out, it is found that 70% of the HRS is due to the TO mode [5].

The observed presence of propagating polar orientational modes in 6 out of 7 simple polar liquids raises two questions. Why are the observed propagating modes polar, and why were they not observed before? Waves in isotropic media are either even or odd under inversion, and HRS is sensitive only to the odd (polar) modes. Polar waves can result from coupled rotations or vibrations of the molecules of the medium [9]. The delocalized polar orientational modes observed here are analogous to the delocalized polar vibrational excitations that have previously been observed by HRS in crystals, glasses and molecular liquids [7]. The reason that these polar orientational modes have not been observed by linear light scattering is that polar modes in isotropic media have the wrong parity to be observed by linear scattering processes. A mutual exclusion rule holds for light scattering from isotropic media, where linear light scattering sees only the acoustic (TA, LA) collective modes, whereas HRS sees only the optic (TO, LO) collective modes. More explicitly for the present case, orientational correlations along $\boldsymbol{K}$ modulate the space-fixed components of the molecular polarizability at twice the polar mode spatial frequency, so destructive interference exactly cancels the linearly scattered wave.

The polar orientational modes considered here differ from molecular orientational motions coupled to local shear flows, previously observed in viscoelastic liquids by depolarized linear light scattering spectroscopy [2,10,11]. Shear strains in a fluid are relieved by both collective molecular reorientation and diffusion, and the orientation-flow coupling for anisotropic molecules leads to a very characteristic light scattering spectrum. Highly damped shear waves with frequency ≈ 0.5 GHz and decay time ≈ 30 ps (decay length ≈ 5 nm) are observed in a wide range

of liquids [10], but oscillatory transverse shear waves are observed only for highly supercooled viscous liquids [11]. For usual liquids the shear modes do not impart long range molecular orientational correlations.

The TO polar orientational mode observed at ± 2 cm^{-1} in the HRS spectrum of liquid acetonitrile [5] has a frequency $10 \times$ larger than that for compressional (LA) sound waves [12] and $100 \times$ larger than that for typical shear (TA) waves observed by linear light scattering at 90°. Orientational correlations on a length scale comparable to the wavelength of the polar mode (≈ 300 nm) are implied by the observed HRS angular and polarization dependence. Polar orientation modes in liquids are expected to have special properties similar to those of polar vibrations in crystals [7,9,13]. Lattice vibrations which carry an electric dipole moment have radically different properties from nonpolar vibrations since the dipole moment couples the lattice vibrations to the radiation field in the crystal to form mixed excitation modes, part phonon and part photon, which have a characteristic dispersion relation and are known as polaritons [13].

The observations reported here show that polar orientation modes which carry long-range orientational correlations are present in many liquids, but further study is needed to determine the properties of these modes. HRS measurements can characterize the frequency, amplitude and damping of these propagating orientational modes, which will allow one to assess their contribution to the structure and transport properties of simple liquids. In particular, long-range structural and dynamic correlations in bulk water mediated by these propagating modes may be important in a wide range of aqueous systems.

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